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Coordination Compounds of Alkali Metal Tetrahydroborates with Ethers and Amines[‡]

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Dedicated to Professor Dr. G. Schmid on the occasion of his 70th birthday

Keywords: Alkali metals / Hydroborates / Amines / X-ray structures

The crystal structure of $LiBH_4(thf)$ is of the same type as that of $LiBH_4(OEt_2)$ in that it forms double chains containing seven-coordinate Li atoms and BH_4 groups where one H atom coordinates to three Li atoms. In addition, three H atoms form Li–H–B bridges to three different Li atoms. $(NaBH_4)_2$(triglyme) shows a sheet structure with eight-coordinate Na atoms (2 O and 6 H atoms). All H atoms of the BH_4 groups are in bridging positions ($1\mu_3{}^2$ and $3\mu_2{}^1$ types) and each triglyme molecule acts as a tris(bidentate) ligand. A more precise structure determination is reported for $NaBH_4$(15-crown-5), which contains an asymmetric tridentate BH_4 group. The compound crystallizes with half a molecule of pyridine. A tridentate BH_4 group is also present in KBH_4(18-crown-6). In contrast, crystallization of $NaBH_4$(18-crown-6) from pyridine gives the salt $[Na(py)_2(18\text{-crown-}6)]BH_4$. The crown ether complex $KH_2BC_5H_{10}$(18-crown-6) binds through its BH hydrogen atoms to the K atom and there is also a weak K···H–C interaction. In contrast to the bidentate BH_4 group in $LiBH_4(py)_3$, the BH_4 group in $LiBH_4(py\text{-}4\text{-}Me)_3$ is tridentate. $LiBH_4$ reacts with py-2-Me to produce $LiBH_4(py\text{-}2\text{-}Me)_2$, which is dimeric in the solid state with BH_4 groups bonding to the Li atoms in a $\mu_3{}^2/\mu_2{}^2$ manner. The reaction of $LiBH_4$ with 2-aminopyridine in THF gives the complex $LiBH_4(thf)_2(py\text{-}2\text{-}NH_2)$ in which only the pyridine N atom coordinates to the Li atom. $NaBH_4$ crystallizes from pyridine as $NaBH_4(py)_3$, which has a chain structure in the solid state where the BH_4 groups show one three-coordinate H atom of the $\mu_3{}^2$ type and two two-coordinate H atoms of the $\mu_2{}^2$ type. The 1:1 dialkylamine complexes of $LiBH_4$ with $HNiPr_2$ and $HNiBu_2$ have different structures. The former shows a chain structure with BH_4 groups bridging two Li atoms with bridges of the $\mu_3{}^2$ and $\mu_2{}^2$ type, whereas the latter compound forms double strands with one $\mu_4{}^3$- and $\mu_2{}^3$-coordinated H atoms. $NaBH_4(morpholine)_2$ forms a three-dimensional structure with four different Na atoms linked by BH_4 groups in a rather unusual manner – they exhibit mono-, bi-, and tridentate functions. $LiBH_4$ adds $MeHN\text{-}NH_2$ in a 2:3 ratio to form the salt $[Li_2(H_2N\text{-}NHMe)_3](BH_4)_2$, which contains chains of $[Li_2(H_2N\text{-}NHMe)_3]^{2+}$ cations separated from $BH_4{}^-$ anions. In contrast, $LiBH_4$ reacts with $PhNH\text{-}NH_2$ to give the adduct $LiBH_4(H_2N\text{-}NHPh)_2$, which associates into chains containing $H_2BH_2LiH_2BH_2Li$ units.

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Introduction

Amongst the alkali metal tetrahydroborates $LiBH_4$ most readily forms coordination compounds with ethers or amines. No adducts of $CsBH_4$ or $RbBH_4$ with ethers or amines have been reported to date,[1] and only crown ether complexes of $NaBH_4$,[1] and more recently of KBH_4,[2] have been described besides the crystal structures of $NaBH_4$(diglyme)[3] and $NaBH_4$(15-crown-5).[4] The crystal structures of $LiBH_4(OEt_2)$,[5,6] $LiBH_4(MeOtBu)$,[6] $LiBH_4(thf)_3$,[6] $LiBH_4(DME)$,[6] $LiBH_4$(dioxane),[6] $LiBH_4$(dioxolane),[6] $LiBH_4$(15-crown-5),[7] and $(LiBH_4)_2$(18-crown-6)[7] show that they can be mono-, di-, or even polynuclear in the solid state.

Only a few coordination compounds of $NaBH_4$ with amines have been well characterized, one example being $[NaBH_4(MeNCH_2CH_2)_3]_4$.[8] $LiBH_4$, however, forms many well-defined coordination compounds with amines. Thus, while the mononuclear species contain di- or tridentate BH_4 groups more complex patterns are observed for di- or even polynuclear species, in which the BH_4 group can bind to as many as three Li atoms. The hydrogen atoms in these cases are two-, three-, and even four-coordinate. The formation of "ate" complexes has also been reported.[9] The structural type formed depends on the $LiBH_4$/ligand ratio, the steric requirements of the ligand, and on the type of ligand, and all these factors also influence whether the BH_4 group is

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mono-, di-, or tridentate in mononuclear adducts. This paper describes new coordination compounds of $LiBH_4$, $NaBH_4$, and KBH_4 with ethers and amines.

Results and Discussion

Synthesis

The coordination compounds **1**–**15** were prepared by adding the ligand to a thf solution of the respective alkali metal tetrahydroborate, or to a pyridine solution of $NaBH_4$ or KBH_4. The addition of methylcyclohexane often proved helpful for the crystallization process. Single crystals of **1**–**15** were obtained for X-ray structure determinations.

$LiBH_4$(thf) **1**	$NaBH_4$(triglyme) **2**	$NaBH_4$(15-crown-5)($py_{0.5}$) **3**
[Na(18-crown-6)(py_2)](BH_4)$_2$ **4**	KBH_4(18-crown-6) **5**	KB($H_2B_{c5}H_{10}$)(18-crown-6) **6**
$LiBH_4$(py-4-Me)$_3$ **7**	$LiBH_4$[(py-2-Me)$_2$]$_2$ **8**	$LiBH_4$(thf)$_2$(py-2-NH_2) **9**
$NaBH_4$(py)$_3$ **10**	$LiBH_4$(HN*i*Pr_2) **11**	$LiBH_4$(HN*i*Bu_2) **12**
$NaBH_4$(morpholine)$_2$ **13**	[Li_2(MeHN-NH_2)$_3$ (BH_4)$_2$] **14**	$LiBH_4$(H_2N-NHPh)$_2$ **15**

Coordination Compounds of Alkali Metal Tetrahydroborates with Ethers

Lithium tetrahydroborate forms three THF adducts: $LiBH_4$(thf), $LiBH_4$(thf)$_2$, and $LiBH_4$(thf)$_3$,[1] although only the structure of $LiBH_4$(thf)$_3$ has been determined to date.[6] It is a mononuclear molecular compound with a hexacoordinate Li atom and a tridentate BH_4 ($3\mu_2{}^1$) group.[10] The other two solvates are not likely to be mononuclear in the solid state: $LiBH_4$(thf)$_2$ may be dimeric while $LiBH_4$(thf) may be polymeric like $LiBH_4$(OEt_2) in the solid state.[5,6]

We obtained single crystals of $LiBH_4$(thf) (**1**) from a highly concentrated THF solution of $LiBH_4$ by adding methylcyclohexane. The compound crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$. Figure 1 shows the asymmetric unit, which contains a three-coordinate Li atom. This unit is connected by two types of Li–H–B bridges to form parallel strands along the *c* axis. Figure 2 shows a section of one of these strands. The Li atoms in these strands are coordinated to one oxygen atom and six H atoms, with Li–H distances ranging from 1.93 to 2.31 Å. The Li1–O1 bond length is 1.934(5) Å while the Li···B distances vary from 2.497(5) (Li1···B1A) to 2.510(7) Å (Li1A···B1) and 2.556(7) Å (Li1A···B1E). The longest Li–H distances are to the four-coordinate H atom ($\mu_4{}^3$ type)[10] which binds to the boron atom and to three Li atoms. This type of bonding has already been observed in $LiBH_4$(OEt_2).[5,6]

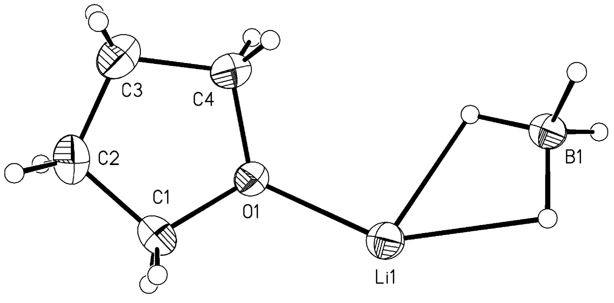

Figure 1. ORTEP plot of the asymmetric unit of $LiBH_4$(thf) (**1**). Selected bond lengths [Å] and angles [°]: Li1···B1 2.497(5), Li1–O1 1.934(5), Li1–HC 2.06(2), Li1–HD 2.01(2), B1–Hc 1.16(2), B1–HB 1.12(2), B1–HA 1.18(2), B1–HD 1.05(2), O1–C1 1.432(3), O1–C4 1.428(4); O1–Li1–B1 121.0(2), O1–Li1–B1A 113.0(3), Li1–O1–C1 119.5(2), Li1–O1–C4 121.8(2), C1–O1–C4 107.8(2), Ha–B1–Hb 105.7(8), Ha–B1–Hc 108.3(8), Ha–B1–Hd 108.8(8), Hb–B1–Hc 105.7(8), Hb–B1–Hd 112.9(8), Hc–B1–Hd 106.0(8), Li1–Hc–B1 97.7(9), Li1–Hd–B1 104.8(9), Li1–Hc–Li1A 97.9(7), Li1–Hc–B 1 97.7(5), Li1A–Hc–B1 86.0(5), Li1–Hd–B1a 104.8(5), Hc–Li1–Hd 51.2(5), Hc–Li1–O1 147.7(5), Hd–Li1–O1 97.7(6).

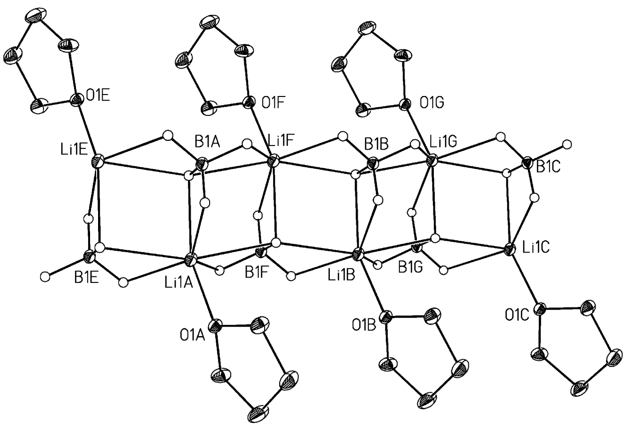

Figure 2. Part of a strand of polymeric $LiBH_4$(thf) (**1**) showing the seven-coordinate Li atoms and the four-coordinate H atom. Typical bond lengths [Å] for the four-coordinate H atom: Li1G–Hcb 2.066(9), Li1B–Hcb 2.311(9), Li1F–Hcb 2.289(8), B1b–Hcb 1.155(2). Additional data are listed in the legend of Figure 1.

($NaBH_4$)$_2$(triglyme) (**2**) possesses a rather unusual structure. It crystallizes in the monoclinic system, space group *C*2/*c* with $Z = 4$. Figure 3 shows the atoms in the asymmetric unit. While atom Na1 is located in a general position, Na2 is found, like B2, on a mirror plane. Figure 4 shows part of the resulting sheet structure. It can be seen that atoms Na1 and Na2 are coordinated by two O atoms and six H atoms. There are two types of BH_4 groups. One type forms two hydrogen bridges to two Na atoms ($\mu_3{}^2$ type) and three single hydrogen bridges to three different Na atoms ($\mu_2{}^3$ type), whereas the other BH_4 group exhibits two hydrogen bridges of the $\mu_3{}^2$ type and two single H bridges to two different Na atoms ($\mu_2{}^2$ type). The hydrogen atoms of three BH_4 groups coordinate to one Na atom. The eight-coordinate atom Na2 forms two Na–O bonds, one with the oxygen atom of a methoxy group and the other with its neighboring O atom. This part of the molecule acts as a bidentate chelating ligand. The two central O atoms chelate to atom

Na1 but they both also coordinate to two different Na2 atoms, both of which are also bonded to a methoxy group of the triglyme molecule. Thus, the central O atoms of the triglyme molecules are four-coordinate, which means that the triglyme molecule acts as a tris(bidentate) ligand.

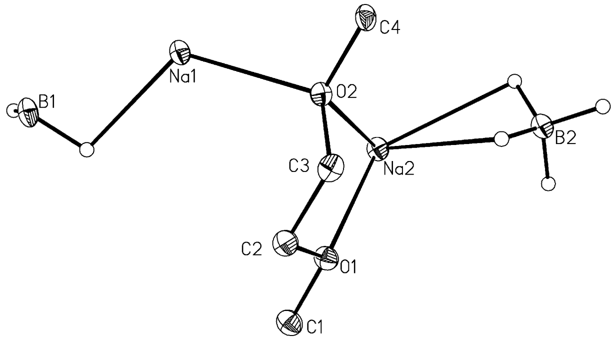

Figure 3. Atoms of $(NaBH_4)_2$(triglyme) (**2**) in the asymmetric unit. Selected bond lengths [Å] and angles [°]: Na1–O2 2.435(1), Na2–O2 2.616(1), Na2–O1 2.372(1), Na2–B2 2.830(2), Na1$\cdots$B1 2.807(2); Na–O2–Na2 103.32(3), O2–Na2–B2 94.19(4), O1–Na2–O2 68.57(3), Na2–O2–C3 103.12(6), Na2–O2–C4 114.64(7), Na1–O2–C3 103.12(6), NA1–O2–C4 109.24(8).

Crown ether complexes of $NaBH_4$ and KBH_4 have already been reported.[1,2,7] They were characterized by elemental analysis, electrical conductivity in solution, and IR spectroscopy.[11] Gorbunov et al.[4] isolated tiny single crystals of $NaBH_4$(15-crown-5). Refinement of its crystal structure converged at $R_1 = 0.117$, which is why the hydrogen atoms around the boron atom could not be located. The question remains as to whether the BH_4 group coordinates to the Na atom or not. We isolated well shaped crystals after adding pyridine to a mixture of $NaBH_4$ and 15-crown-5. The compound crystallizes as $NaBH_4(15\text{-crown-}5)(py)_{0.5}$ (**3**). As depicted in Figure 5, this crown ether complex forms molecular units where a three-coordinate BH_4 group coordinates to the sodium center in a distorted manner. The B–H bond lengths of the bridging H atoms are 1.15(2) Å on average, with the longest and the shortest B–H bonds being those to the nonbridging H atoms H1A (1.16 Å) and H1D (1.04 Å), respectively. The Na–H bond lengths show that the BH_4 group is asymmetrically bonded to the Na atom

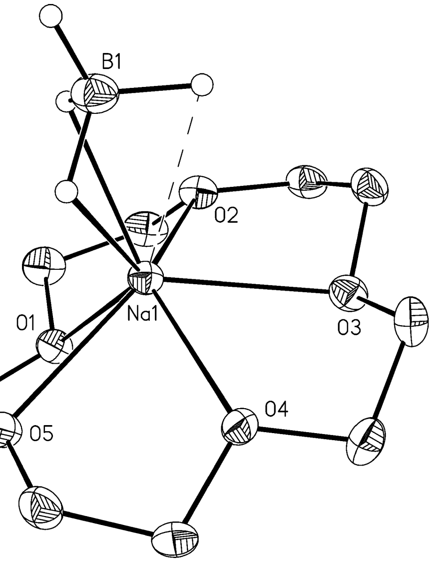

Figure 5. ORTEP plot of $NaBH_4(15\text{-crown-}5)(NC_6H_5)_{0.5}$ (**3**). The pyridine part is not shown. The BH_4 group binds asymmetrically to the Na atom (see dashed line). Selected bond lengths [Å]: Na1–O1 2.401(4); Na1–O2 2.473(3), Na1–O3 2.479(3), Na1–O4 2.379(3), Na1–O5 2.462(3), Na1–B1 2.659(3), B1–Ht 1.04(2), B1–Htb 1.16(2), B1–Ha 1.15(2), B1–Hb 1.17(2), Na1–Ha 2.28(2), Na1–Hb 2.42, Na1–Htb 2.74(2).

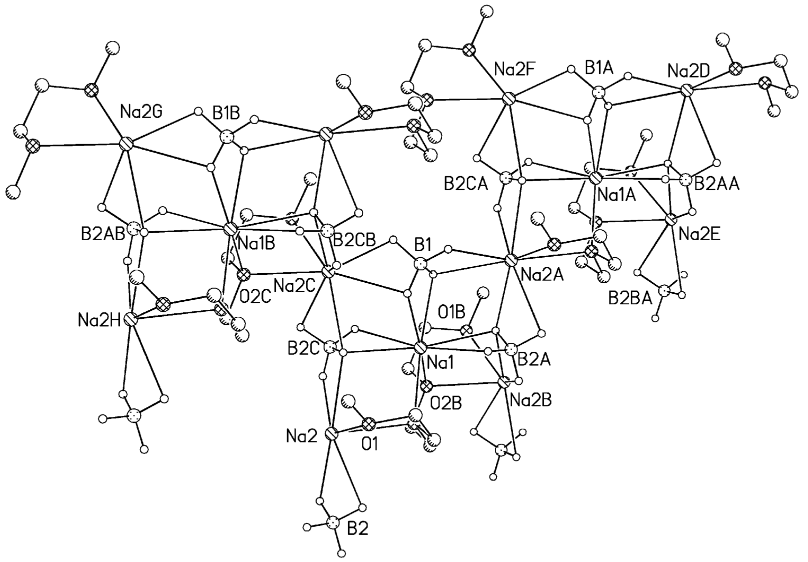

Figure 4. Part of the sheet structure of compound **2**. Selected bond lengths [Å] and angles [°]: Na1–B2B 2.860(1), Na1–B2C 2.860(1), Na2–B1D 2.881(6), Na2–B2C 2.905(2); O2–Na1–B1 143.83(2), O2–Na1–B2B 93.05(4), O2–Na1–B2C 86.17(4), B–Na1–B2C 90.48, B2B–Na1–B2C 179.03(6), O1–Na2–B1D 89.61(5), O2–Na2–B2C 82.04(3), O2–Na2–B1D 175.99(4).

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as there are two shorter Na–H distances [2.42 and 2.28(2) Å] and a significantly longer one [2.74(2) Å]. The Na–O bond lengths range from 2.379(3) (Na1–O4) to 2.479(3) Å (Na1–O3). The Na atom is therefore eight-coordinate. The pyridine molecule does not coordinate and is present in the crystal in a site-disordered position.

A different result was obtained with $NaBH_4$ and 18-crown-6 as the crown ether. The crystals that separate from the pyridine solution of $NaBH_4$ after addition of the crown ether have the composition $NaBH_4(py)_2$(18-crown-6) (**4**) and a monoclinic unit cell (space group $P2_1/c$, $Z = 2$). The sodium atom is located on an inversion center. As shown in Figure 6, the compound is composed of an $[Na(py)_2$(18-crown-6)$]^+$ cation and a BH_4^- anion. There are four long [2.743(1) and 2.807(1) Å] and two short Na–O bond lengths [2.424(2) Å for Na1–O1/1A] in the cation and the Na–N bond length is shorter [2.423(2) Å] than the Na–O distances, most likely due to the presence of a three-coordinate N atom. The B atom of the BH_4 group is also located on an inversion center, which causes a problem for the sites of the B–H hydrogen atoms. The Fourier map shows three residual electron densities that are acceptable for B–H distances but the inversion center generates three more peaks, although not in a pseudo-octahedral array, which is required for a site-disordered BH_4 group. We therefore show only the B atom in Figure 6.

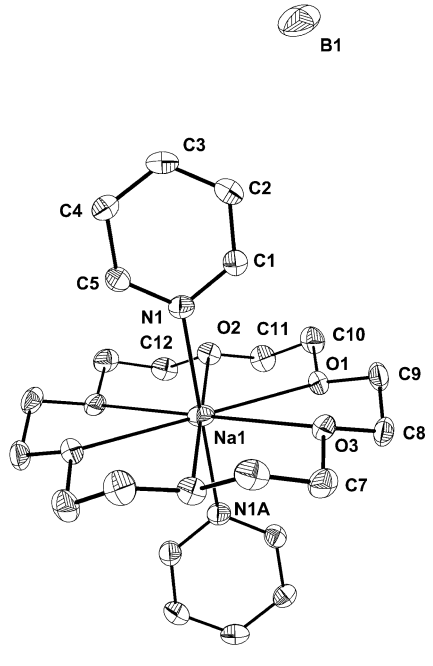

Figure 6. ORTEP plot of $[Na(18\text{-crown-}6)(NC_5H_5)_2]BH_4$ (**4**). Only the B atom of the BH_4 group is shown (see text). Selected bond lengths [Å] and angles [°]: Na1–N1 2.423(2), Na1–O1 2.743(1), Na1–O2 2.732(1), Na1–O3 2.807(1), O1–C9 1.419(3), O1–C10 1.421(3), O2–C11 1.410(3), O2–C12 1.426(3), O3–C7 1.416(3), O3–C8 1.422(2); N1A–Na1–N1 180.0, N1–Na1–O1 95.54(6), N1–Na1–O2 90.03(6), N1–Na1–O3 85.45(5), O2–Na1–O1 61.37(4), O1–Na1–O3 58.06(4), O2–Na1–O3 118.38(4), O1A–Na1–O3 121.94(4), C1–N1 –Na1 117.7(1), C5–N1–Na1 123.5(2).

Coordination compounds of KBH_4 are difficult to prepare because its solubility in ethers and amines is poor. However, addition of pyridine to a suspension of KBH_4 in 18-crown-6 caused the potassium salt to dissolve. Colorless needles of KBH_4(18-crown-6) (**5**) separated from the solution on cooling. They are orthorhombic (space group $P2_12_12_1$). Figure 7 shows that the BH_4 group of **5** acts as a tridentate ligand with average K–H distances of 2.74(8) Å. The B–H bond length to the terminal hydrogen atom is the shortest [0.98(6) Å], with the others ranging from 1.02(8) to 1.11(8) Å. The K–O distances range from 2.752(4) (K1–O3) to 2.911(4) Å (K1–O2), and the K1–B1 distance [2.964(9) Å] is 0.305 Å longer than the Na–B distance in $NaBH_4$(15-crown-5)$(py)_{0.5}$. This is not unexpected as the ionic radius of five-coordinate Na^+ is 1.16 Å and that of nine-coordinate K^+ is 1.69 Å. In this case the observed difference in the M–B distances is significantly shorter than the calculated difference of 0.53 Å. The average M–O distance for $NaBH_4$(15-crown-5) is 2.539 Å whereas for KBH_4(18-crown-6) the value is 2.809 Å. This difference of distances is 0.310 Å, which is still shorter than the calculated value but is close to the difference in the M–B distances.

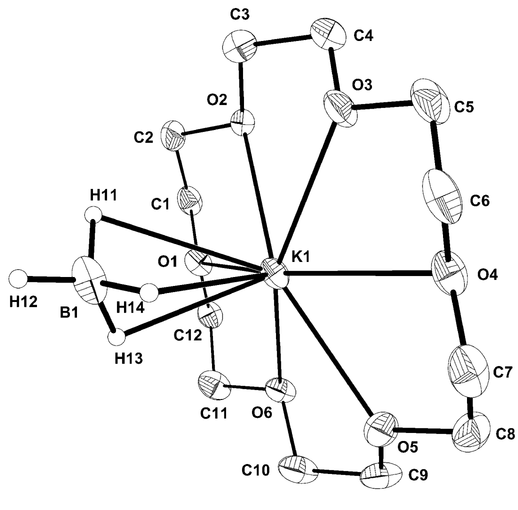

Figure 7. ORTEP plot of KBH_4(18-crown-6) (**5**). Selected bond lengths [Å] and angles [°]: K1–B1 2.964(9), K1–H11 2.85(6), K1–H13 2.61(8), K1–H14 2.77(7), B1–H11 1.11(7), B1–H12 0.98(6), B1–H13 1.02(7), B1–H14 1.08(7), K1–O1 2.808(4), K1–O2 2.911(4), K1–O3 2.752(4), K1–O4 2.895(4), K1–O5 2.849(4), K1–O6 2.879(4), O1–C1 1.396(6), O1–C12 1.408(6), O2–C3 1.401(7), O2–C2 1.443(6),O3–C4 1.404(7),O3–C5 1.430(7), O4–C6 1.403(7), O4–C7 1.429(8), O5–C8 1.422(8), O5–C9 1.410(7), O6–C10 1.419(7), O6–C11 1.417(7); H13–K1–H14 31(2), H13–K1–H11 37(2), H14–K1–H11 39(2), H13–K1–O1 86(2), H14–K1–O1 113(2), H13–K1–O2 109(2), H14–K1–O2 109(1), H11–K1–O2 74(1), H11–K1–O4 122(1), H13–K1–O4 118(2), H14–K1–O4 91(1), H11–K1–O(6) 118(1), H13–K1–O4 118(2), H14–K1–O6 119(1), O1–K1–O2 57.8(1), O3–K1–O1 117.1(1), O1–K1–O5 117.1(1), O1–K1–O4 155.6(1), O1–K1–O6 58.99(1), O1–K1–O5 117.1(1), O1–K1–O6 59.0(1).

In contrast to KBH_4, the diorganodihydroborates of potassium are soluble due to their organophilic groups. To the best of our knowledge, only one potassium diorganodihydroborate, namely dimeric $KBH_2t\mathrm{Bu}_2$(PMDTA), has

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been structurally characterized.[13] Addition of 16-crown-8 to a solution of potassium borinatodihydroborate in thf provided crystals of the crown ether complex $K(H_2BC_5H_{10})$(18-crown-6) (**6**), which crystallizes in the triclinic system (space group $P\bar{1}$) with two independent molecules in the asymmetric unit. Because the structural parameters of these two molecules differ only marginally, we will only discuss the data for one of these molecules, whose structure is shown in Figure 8.

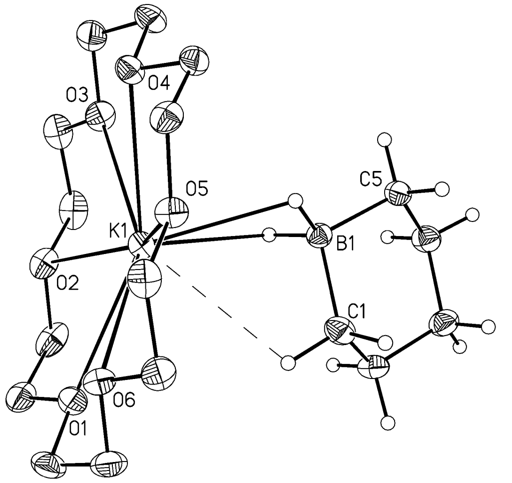

Figure 8. ORTEP plot of $K(H_2BC_5H_{10})$(18-crown-6) (**6**). Selected bond lengths [Å] and angles [°]: K1–O1 2.872(2), K1–O2 2.897(2), K1–O3 2.801(2), K1–O4 2.931(2), K1–O5 2.830(1), K1–O6 2.966(2), K1–B1 3.037(3), K1–H1 2.58(2), K1–H2 2.66(2), K1–H1a 3.07(3), B1–H1 1.19(2), B1–H2 1.14(2), C1–H1A 0.96(2), B1–C1 1.630(4), B1–C5 1.629(3); K1–B1–C1 94.09(1), K1–B1–C5 156.4(2).

There is a close similarity with the structure of KBH_4(18-crown-6) as the potassium ion interacts with three hydrogen atoms. Two stem from the BH_2 group of the dihydroborinate anion and the third one comes from a hydrogen atom of a CH_2 group next to the BH_2 group. This latter interaction is, however, weaker than those with the BH_2 group, as shown by its longer distance [3.07(3) Å for K···H(C)]. The K–H(B) distances are 2.58(2) and 2.66(2) Å and the K–O bond lengths average 2.883(2) Å. This is 0.034 Å longer than for the K–O bonds in KBH_4(18-crown-6) and corresponds to a longer K···B distance which exceeds that in KBH_4(18-crown-6) by 0.073 Å. The presence of an agostic K···H(C) interaction is demonstrated not only by the K···H(C) distance but also by the tilting of the six-membered ring, as shown by the K1–B1–C1 angle of 94.1(1)° compared with the K1–B1–C5 angle of 156.4(2)°. The H–B–H [107(2)°] and C–B–C bond angles [108.7(2)°] are close to that of a regular tetrahedron.

Lithium and Sodium Tetrahydroborate Amine Adducts

The known coordination compounds of $LiBH_4$ with tertiary amines contain pyridines, *N*-methylated enamines (TMEDA or PMDTA), or trialkyltriazines. To the best of our knowledge, only two complexes with secondary amines have been structurally characterized, namely $LiBH_4[HN(CH_2Ph)_2]$ and $LiBH_4(HNC_4H_8)$.[9] The former is a dimer with one $\mu_3{}^2$-(Li_2)H–B and two $\mu_2{}^2$-Li–H–B bonds whereas the latter forms a linear polymer where the BH_4 anion connects three Li atoms in a $\mu_2{}^3$, $\mu_3{}^2$ manner in analogy to $LiBH_4$(TMEDA).[14]

We can now add to the pyridine complexes $LiBH_4(py)_3$ and $LiBH_4(py\text{-}2,4,6\text{-}Me_3)_2$[9] the structures of $LiBH_4(py\text{-}4\text{-}Me)_3$ (**7**), $[LiBH_4(py\text{-}2\text{-}Me)_2]_2$ (**8**), $LiBH_4(thf)_2(py\text{-}2\text{-}NH_2)$ (**9**), and $NaBH_4(py)_3$ (**10**) Figure 9 shows the molecular structure of **7**, which crystallizes in the triclinic system (space group $P\bar{1}$). It is a mononuclear coordination compound with two independent molecules in the unit cell, which differ in the bonding situation for the BH_4 group.

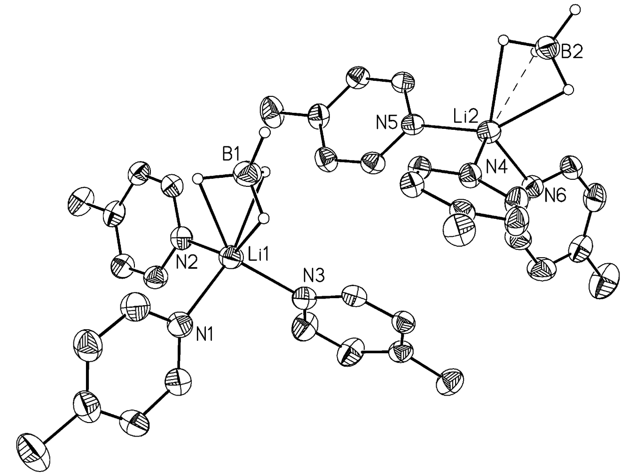

Figure 9. ORTEP plot of the two independent molecules in $LiBH_4(NC_5H_5\text{-}4\text{-}Me)_3$ (**7**). Selected bond lengths [Å] and angles [°]: Li1–N1 2.100(4), Li1–N2 2.092(5), Li1–N3 2.095(4), Li1–B1 2.319(5), Li1–H11 2.10(2)(), Li1–H12 2.20(2), Li1–H13 2.10(2), B1–H11 1.14(3), B1–H12 1.12(3), B1–H13 1.22(4), B1–H14 1.09(4), Li2–N4 2.086(5), Li2–N5 2.079(5), Li2–N6 2.078(4), Li2–B2 2.381(5), B2–H21 1.142, B2–H22 1.065, B2–H23 1.155, B2–H24 1.082, Li2–H21 2.24(2), Li2–H22 2.36(2), Li2–H23 2.15(3), B2–H21 1.14(4), B2–H22 1.07(3), B2–H23 1.16(4), B2–H24 1.08(4); B1–Li1–N1 113.1(2), B1–Li1–N2 112.4(2), B1–Li1–N3 116.4(3), B2–Li2–N4 114.6(2), B2–Li2–N5 118.1(2), B2–Li2–N6 106.5(2).

Molecule A displays an almost perfect tridentate BH_4 group and shows slightly longer Li–N bonds [2.100(4), 2.092(5), and 2.095(4) Å] than the second molecule B, which is characterized by a distorted tridentate BH_4 group [2.086(4), 2.079(5), and 2.078(4) Å]. The Li–B distance in molecule B is longer [2.381(5) Å] than that in molecule A [Li–B = 2.319(5) Å]. The three Li–H bond lengths in molecule A average 2.16(3) Å, whereas molecule B contains two somewhat longer [av. 2.19(3) Å] Li–H bond lengths along with a longer third Li–H bond (2.36 Å). This H atom occupies a position between a bridging and a terminal B–H atom. In both cases the terminal B–H bonds are shorter [1.09(4), 1.08(4) Å] than those in the bridging position.

$LiBH_4(py\text{-}2,4,6\text{-}Me_3)_2$ is unusual because the Li atom is only four-coordinate and shows a bidentate BH_4 group.[9] It was therefore of interest to investigate the steric effect of a single Me group in the *ortho* position of the pyridine li-

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gand. The compound isolated has the composition $LiBH_4(py\text{-}2\text{-}Me)_2$ and crystallizes in the monoclinic system ($P2_1/n$, $Z = 4$) with two dimeric molecules in the unit cell. The Li atoms are six-coordinate, as shown in Figure 10. The two BH_4 groups bridge the two Li atoms by two Li–H(B)–Li bridges of the $\mu_3{}^2$ type and each BH_4 unit forms two single Li–H–B bridges to the two Li atoms ($2\mu_2{}^2$). The Li···B distances are fairly long [2.517(4) and 2.518(4) Å], and the Li–H bond lengths vary from 1.96(1) to 2.13(1) Å. The bond angles at the Li atoms are N1–Li1–N2 = 110.2.(2)°, N2–Li1–B1 = 102.5(2)°, and N2–Li1–B1 123.2(2)°.

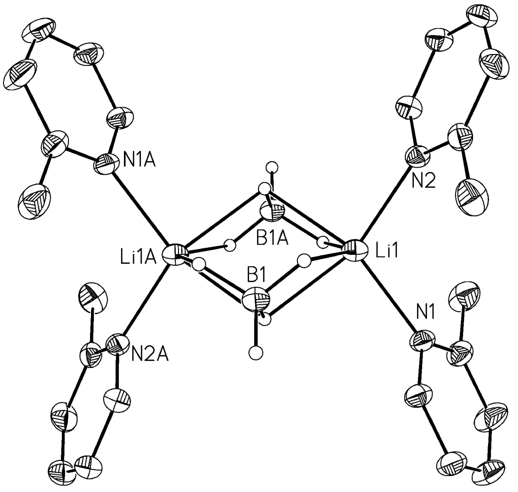

Figure 10. ORTEP plot of $[LiBH_4(py\text{-}2\text{-}Me)_2]_2$ (**8**). Selected bond lengths [Å] and angles [°]: N1–C5 1.341(3), N1–C1 1.342(3), N1–Li1 2.121(4), N2–Li1 2.095(4), Li1–B1 2.517(4), Li1A–B1 2.518(4), Li1–H1 2.134(6), Li1–H2 2.024(8), Li1–H1A 2.184(6), Li1–H3A 1.965(4), H1–Li1A 2.184(7), B1–H1 1.45(2) ($\mu_3{}^2$), B1–H2 1.12(2) ($\mu_2{}^1$), B1–H3 1.18(2) ($\mu_2{}^1$), B1–H4 1.15(2) (t) (t = terminal); C1–N1–C5 116.8(2), C5–N1–Li1 128.1(2), C1–N1–Li1 114.7(2) C11–N2–Li1 126.8(2), C7–N2–Li1 115.0(2), H2–B1–H4 108.9(3), H1–B1–H2 108.9(6), H1–B1–H4 109.4(6), H2–B1–H3 108.8(3), H3–B1–H4 112.7(5), H1–B1–H3 108.8(3), H2–Li1–N2 98.8(2), H2–Li1–N1 107.4(2), H3–Li1–N2 105.9(2), H3A–Li1–N1 98.0(3), N1–Li1–N2 110.2(2), N1–B1–Li1 102.5(2), N2–Li1–B1 123.2(2), Li1–H1–Li1A 102.5(5), B1–H3–Li1A 103.5(6), B1–H2–Li1 102.7(5).

2-Aminopyridine is related to py-2-Me, and here the question arises as to whether this ligand will bind by its amino group to $LiBH_4$ or via the pyridine nitrogen atom, or both. The reaction of this ligand with $LiBH_4$ in THF led to crystals with the composition $LiBH_4(thf)_2(py\text{-}2\text{-}NH_2)$. The crystals are monoclinic (space group $P2_1$) with two independent molecules in the asymmetric unit. The BH_4 group binds in a bidentate manner ($2\mu_2{}^1$) to the Li atom, and only the pyridine nitrogen atom coordinates to Li. Figure 11 shows only one of the two independent molecules, but we list selected bonding parameters for both.

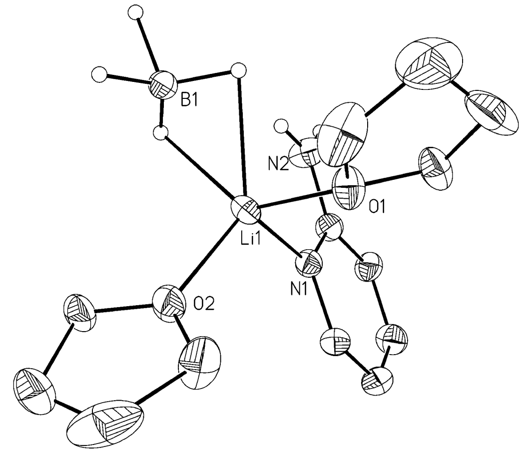

Figure 11. ORTEP plot of $LiBH_4(thf)_2(py\text{-}2\text{-}NH_2)$ (**9**). Selected bond lengths [Å] and angles [°]: Li1–O1 1.97(1), Li1–O2 2.101(1), Li1–B1 2.41(1), N1–C1 1.340(8), N2–C1 1.340(8), Li2–O3 1.94(1), Li2–O4 1.97(1), Li2–N3 2.09(1), Li2–B2 2.41(1), N3–C8 1.08(5) 1.335(8), N3–C9 1.395(8), B1–H1a 1.23(6), B1–H1t 1.08(5), B2–H2a 1.08(4), B2–H2b 1.14(5), B2–H2f 0.95(5), B2–H2g 1.28(6); O1–Li1–O2 104.6(5), O1–Li1–N1 99.5(5), O2–Li1–N1 110.0(5), O1–Li1–B1 115.1(4), O3–Li2–O4 99.0(6), O3–Li1–N1 100–6(5), O2–Li2–N3 106.7(5), O2–Li2B2 114.4(6), O2–Li–B2 113.4(6).

$NaBH_4$ crystallizes from its pyridine solution as $NaBH_4(py)_3$ (**10**). Figure 12 depicts the atoms in the asymmetric unit. The Na atom is pentacoordinate, and the BH_4 groups function as bidentate ligands. The Na1–N bonds are essentially equal for N1 and N2 [2.491(2) and 2.504(2) Å] while the distance to N3 is slightly shorter [2.468(2) Å]. The Na–H distances are significantly different, ranging from 2.48(3) to 2.62(3) Å. A rather long Na–B distance suggests that the Na atom is not coordinatively saturated. Indeed, the mononuclear unit associates in the unit cell into chains (Figure 13) containing seven-coordinate Na atoms. The BH_4 groups coordinate to the Na atoms via one $\mu_3{}^2$- and

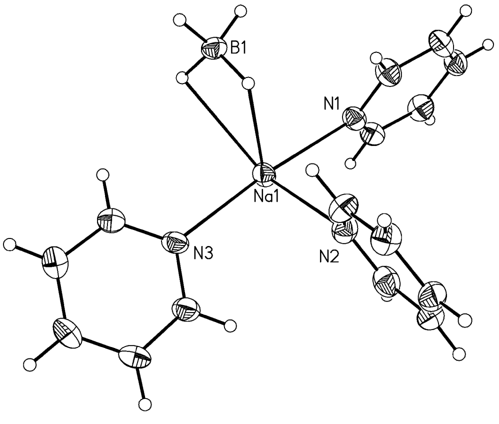

Figure 12. The asymmetric unit of $NaBH_4(py)_3$ (**10**)). Selected bond lengths [Å] and angles [°]: Na1 –N1 2.491(2), Na1–N2 2.504(2), Na1–N3 2.468(2), Na1–B1 2.927(3), Na1–H11 2.53(3), Na1–H11 2.62(3), Na1–H12 2.61(3), Na1–H13 2.48(3), B1–H11 1.13(3), B1–H12 1.05(3), B1–H13 1.09(4), B1–H14 1.06(4), H13–Na1B, 2.48(3); N3–Na1–N1 175.04(7), N3–Na1–N2 85.18(7), N1–Na1–N2 90.69(6), N3–Na1–H13A 96.5(8), H13A–Na1–N1 81.1(8), H13A–Na1–N2 94.8(8), N3–Na1–H11 88.0(7), N1–Na1–H11 94.3(7), N3–Na1–H11A 88.2(6), N1–Na1–H11A 92.7(6), N2–Na1–H12 122.9(8), H11–Na1–H11A 141(2), H13A–Na1–H12 141(1), H13A–Na1–H11 175(1), H13A–Na1–H11A 41(1), N2–Na1–H11A 133.8(6), N3–Na1–H12 81.1(7), N1–Na1–H12 103.5(7), H11–Na1–H12 41(1), B1–Na1–B1A 141.61(6), H12–B1–H11 110(2), H13–B1–H11 106(2), H14–B1–H11 115(3), H12–B1–H13 105(2), H12–B1–H14 113(3), H14–B1–H13 107(3), H11–Na1–B1A 62.5(7), H12–Na1–B1A 122.1(8), B1–H11–Na1B 96(1).

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two μ_2^2-Na–H–B bridges, which leaves a single terminal hydrogen atom non-coordinated. The Na–B distances are 2.927(3) and 2.958(3) Å.

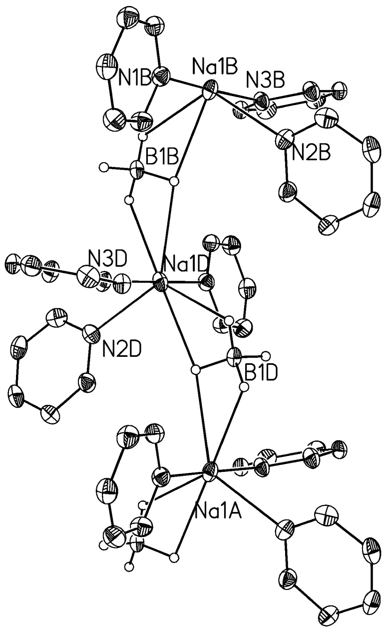

Figure 13. Part of the chain of compound **10** showing the asymmetric unit of NaBH$_4$·3py. Selected bond distances [Å] and angles [°]: Na1D–B1A 2.958(3), Na1D–B1D 2.927(3), Na1D–H13A 2.46(3), Na1D–H11D 2.53(3), Na1D–H11A 2.62(3), Na1D–H11A 2.62(3), Na1D–H11A 2.62(3), Na1D–H11A 2.62(3), Na1D–H11A 2.62(3), Na1D–H11A 2.62(3), Na1D–H11A 2.62(3); B1A–Na1D–B1D 141.6(7), Na1A–H11A–Na1D 164.5(8), Na1A–H11A–B1A 99.3(8), B1A–H11A–Na1D 96.2(8).

Bis(isopropyl)amine and bis(isobutyl)amine form 1:1 complexes with LiBH$_4$. LiBH$_4$[HN(CHMe$_2$)] (**11**) crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. Figure 14 depicts the asymmetric unit, which immediately indicates that this unit must interact with neighboring molecules. Figure 15 demonstrates the function of the BH$_4$ groups, which interact with only two Li atoms via one μ_3^2 and two μ_2^2 bridges. The Li atom is five-coordinate and is located in the center of a plane containing two B atoms and one N atom (sum of bond angles = 360°). The terminal B–H bond is the shortest [1.04(3) Å] and the μ_2-H hydrogens forms the longest B–H bonds [1.17 and 1.11(3) Å], while the μ_3^2-type B–H bond turns out to be short [1.07(3) Å].

Crystals of compound LiBH$_4$[HN(*i*Bu)$_2$] (**12**) are monoclinic (space group $P2_2/c$ and $Z = 8$). Figure 16 shows that there are two independent molecules in the asymmetric unit, which join each other to form a double-stranded chain (Figure 17) with seven-coordinate Li atoms. Each Li atom coordinates to H atoms from three different BH$_4$ groups, each of which has a terminal hydrogen atom, two hydrogen atoms of the μ_3^2-type, which coordinate to the boron atom and two Li atoms, and one μ_2^1-type bridge bond. This bonding pattern of the BH$_4$ units is new for amine complexes of LiBH$_4$. The N and B atoms about each Li atom are arranged in a distorted tetrahedral array with bond angles ranging from 93.8° to 125.0°.

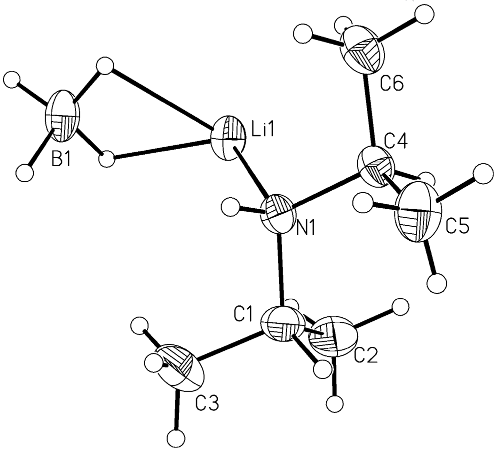

Figure 14. ORTEP plot of the atoms in the asymmetric unit of LiBH$_4$(HN*i*Pr$_2$) (**11**). Selected bond lengths [Å] and angles [°]: Li1–B1 2.358(3), Li1–N1 2.076(3), Li1–H1A 1.93(1), Li1–H1B 2.03(1), B1–H1A 1.06(), B1–H1B 1.08(2), B1–H1C 1.04(2), B1–H1D 1.17(2); C1–N1–Li1 113.1(1), C4–N1–Li1 111.0(1), N1–Li1–B1 111.1(1), N1–Li1–B1A 122.3(1), B1–Li1–B1A 125.6(1), H1A–B1–H1B 111.2(8), H1A–B1–H1C 109.9(8), H1A–B1–H1D 110.1(8), H1B–B1–H1C 103.9(8), H1B–B1–H1D 111.5(8).

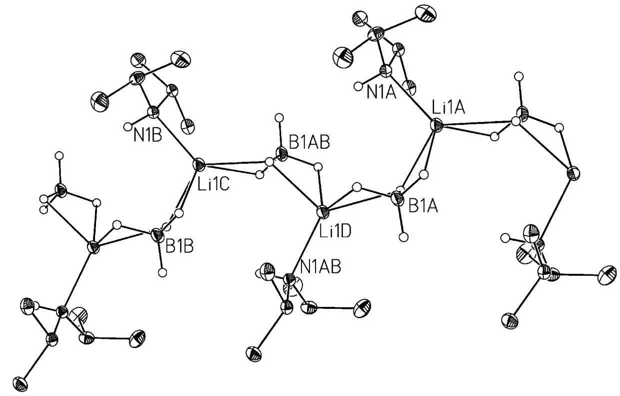

Figure 15. Part of the chain structure of compound **11**.

The shortest bond is the Li1–N1 bond [2.091(7) Å], while the Li1–B distances are 2.542(8) (B1), 2.604(9) (B1A), and 2.643(8) Å (B1B). The corresponding distances to Li2 are: Li2–N2 = 2.086(7), Li2–B2 = 2.543(8), Li2–B2A = 2.616(8), and Li2–B1A = 2.635(8) Å. The bonds to the terminal H atoms are short [0.98(4) and 1.09(4) Å], and the Li–H bond lengths vary from 2.06(2) to 2.33(2) Å.

Amongst the coordination compounds of the alkali metal tetrahydroborates compound NaBH$_4$(morpholine)$_2$ (**13**) has a very unique structure in the solid state.[12] This is already evident by looking at the asymmetric unit of this compound, which contains four different Na centers each of which is located in a different environment (Figure 18). Na1 is surrounded by four morpholine molecules, all of which are coordinated to Na1 by their oxygen atoms. Na2 coordinates to one O and two N atoms in a distorted trigonal plane, while Na3 binds to two O atoms and two BH$_4$ groups, both of which interact with Na3 in a bidentate manner. Two BH$_4$ groups are also bonded to atom Na5, but

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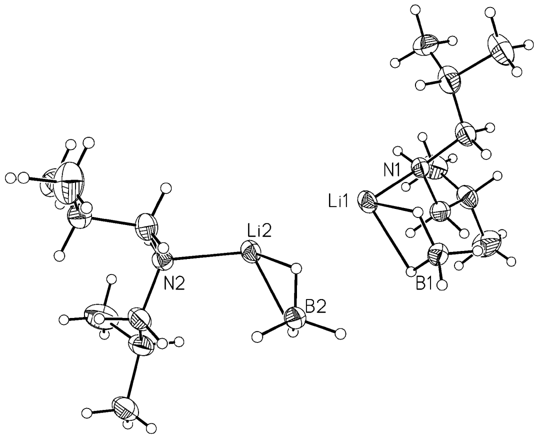

Figure 16. ORTEP plot of the asymmetric unit of LiBH$_4$(HN*i*Bu$_2$) (**12**). Selected bond lengths [Å]: Li1–N1 2.091(7), Li2–N2 2.086(7), N1–C2 1.492(5), N1–C5 1.467(5), N2–C11 1.462(5), N2–C15 1.481(5), B1–H1A 1.10(2), B1–H1B 1.12(2), B1–H1C 0.98(2), B1–H1D 1.14(2), B2–H2G 1.09(2), B2–H2F 1.12(2), B2–H2H 1.09(2), B2–H2E 1.09(2), Li1–H1B 2.13(2), Li1–H1D 2.07(2), Li1–H1BA 2.33(2), Li1–H2A 2.13(2), Li1–H1AA 2.06, Li1–H2EA 2.17(2), Li2–H2F 2.23(2), Li2–H2E 2.18(2), Li2–H2FA 2.26(2), Li2–H2FA 2.02(2), Li2–H1AA 2.18(2), Li2–H1DA 2.29(2).

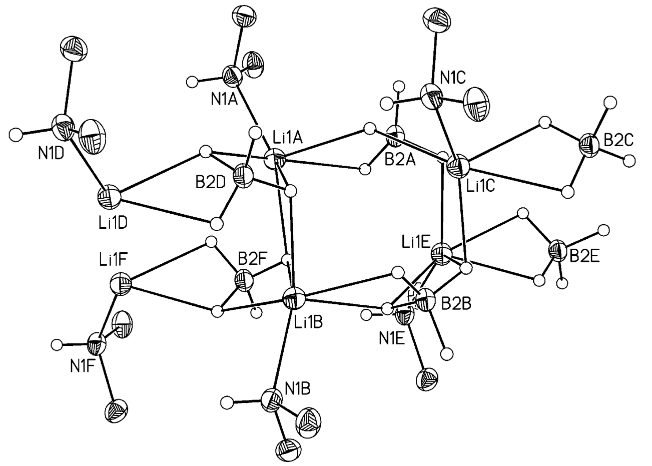

Figure 17. ORTEP plot of part of the double chain of compound **12**. The organo groups (except for two C atoms) have been omitted for clarity: Selected bond distances [Å]: Li1A–B2A = B2F–Li1B 2.643(8), Li1A–B2D 2.543(8).

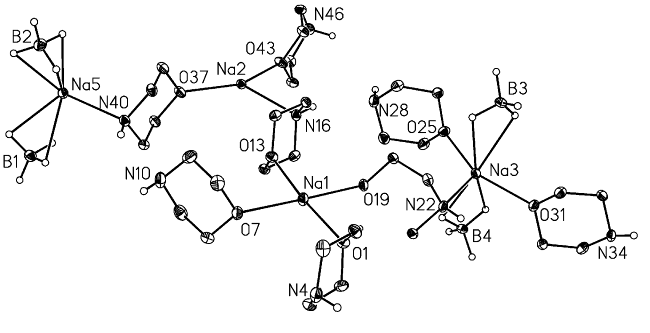

Figure 18. Atoms in the asymmetric unit of NaBH$_4$(morpholine)$_2$ (**13**). Selected bond lengths [Å] and angles [°]: Na1–O1 2.384(2), Na1–O7 2.52(2), Na1–O19 2.445(2), Na1–O13 2.381(2), Na2–N16 2.525(2), Na2–O43 2.344(2), Na2–O37 2.439(2), Na3–O31 2.410(2). Na3–O25. 2.503(2), Na3–N22 2.550(2), Na5–N40 2.538(2), Na5– N34C 2.589(2), Na5–N34C 2.589(2), Na2–B4a 2.957(3), Na2–B3B 2.958(3), Na3–B4 2.907(3), Na3–B3 2.908(3), Na5–B2 2.637(3), Na5–B1 2.642(3), N4–C5 1.458(4), N4–C3 1.458(4), N10–C9 1.453(4), N10–C11 1.466(4), N16–C15 1.469(4), N16–C17 1.471(4), N22–C23 1.465(3), N22–C21 1.468(3), N28–C27 1.461(4), N28–C29 1.464(4), O1–C2 1.427(3), O1–C6 1.428(3), O7–C8 1.439(3), O13–C14 1.434(3), Na1–O1 173.54(8); O12–Na1–O19 86.44(7), O13–Na1–O19 87.10(7), O13–Na1–O7 91.41(7). O1–Na1–O7 95.05(7), O19–Na1–O7 178.50(9), O42–Na2–O37 154.52(9), O43–Na2–N16 87.03(8), O43–Na2–B4 90.11(7), O37–Na2–B4 94.84(7), N16–Na2–B4 102.98(9), O37–Na2–B3 84.77(7), B4–Na2–B3 156.0(1), O31–Na3–O25 149.07(9), O31–Na3–N22 86.21(8), O31–Na3–O25 149.7(1), N40–Na5–N34C 118.75(8), N40–Na5–B2 99.9(1), N40–Na5–B2 99.9(1), B2–Na5–B1 128.3(1).

this time in a tridentate manner. Na5 is also coordinated to one N atom and shares a plane with one nitrogen and two boron atoms. The coordination numbers of the Na atoms in the asymmetric unit are four for Na1, three for Na2, and seven for Na3 and Na5.

Expansion of the atoms in the asymmetric unit generates a three-dimensional array (Figure 19) in which all Na atoms are either six- or seven-coordinate. Na1 is now coordinated to the two hydrogen atoms of two single Na1–H–B bridges that are arranged in a *trans* position at atom Na1. These two H atoms are the terminal H atoms of atoms B1 and B2 of the asymmetric unit. This generates a string of Na5–B2–Na1–B1–Na5–B2 atoms, as shown in Figure 20. Moreover, the two terminal H atoms of the BH$_4$ groups attached by bidentate BH$_4$ groups on atom Na4 in the asymmetric unit are now bonded by additional bidentate bonds to atoms of type Na3, which becomes seven-coordinate (Figure 21). The three-dimensional network is built from the asymmetric units by new Na–H–B bonds. This leads to a unique situation where the BH$_4$ groups interact with the Na centers by mono-, bi-, and tridentate BH bonds (see Figures 20–22) with Na–B distances of 3.38, 2.908, and 2.640 Å.

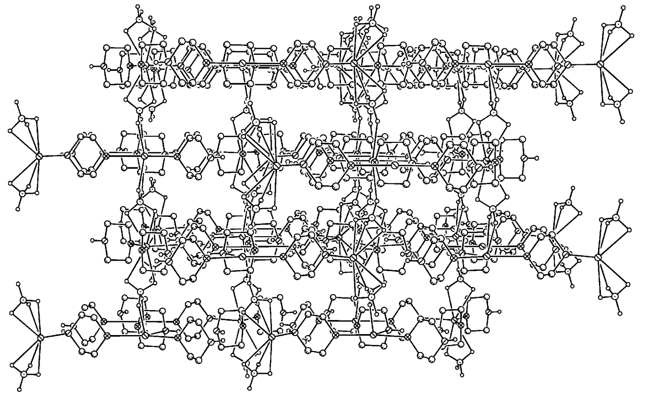

Figure 19. View down the *b* axis of the unit cell of compound **13** showing the three-dimensional network of atoms.

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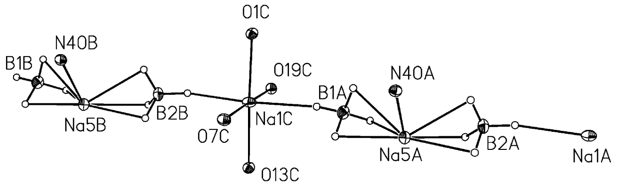

Figure 20. Coordination of the atoms around Na1 and Na5 showing the single H bridge between Na and B and the tridentate coordination of the BH_4 groups with atoms Na5 in compound **13**. The Na1–H–B bond angles are 155.2(4)°.

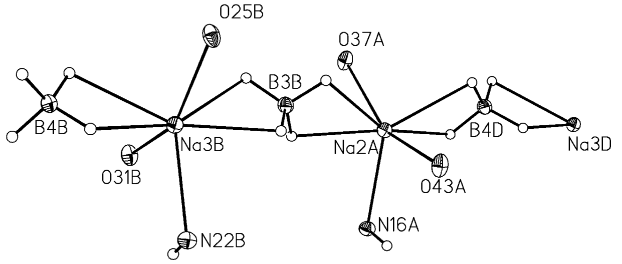

Figure 21. Double bidentate Na–H–B bridges in **13** between atoms Na2 and Na3. Both Na atoms are seven-coordinate.

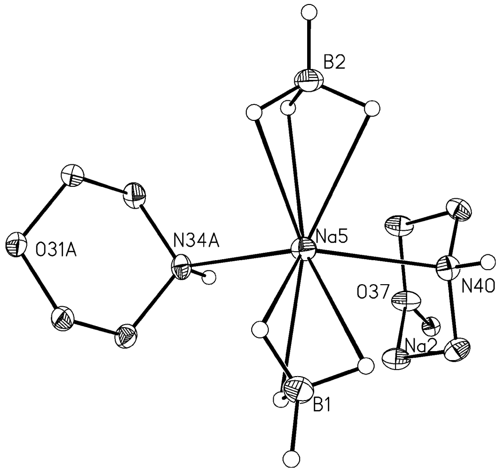

Figure 22. The tridentate Na–H–B bridges at atom Na5 in compound **13**.

The arrangement of the BH_4 groups in this compound suggests a formal BH_4 group transfer of the type

$2\ NaBH_4 \rightarrow Na^+ + [Na(BH_4)_2]^-$

However, each Na atom interacts with H atoms of BH_4 groups in addition to the O and N atoms. The weakest bond is formed from the unique H atom coordinating to atom Na1. This compound demonstrates again that the BH_4 group is a rather unusual and most interesting ligand.

Lithium Tetrahydroborate Hydrazine Adducts

Hydrazines offer two Lewis base centers and could behave differently to amines. The reaction of $LiBH_4$ with $MeHN\text{-}NH_2$ in a 1:1 ratio in thf yields monoclinic crystals of the composition $Li_2(BH_4)_2(MeHN\text{-}NH_2)_3$ (**14**; space group *C*2/*c*, *Z* = 8) with two independent molecules in the unit cell. Atom Li1 sits on a twofold axis, while Li2 occupies a general position. B1 also occupies a special position and B2 is located in a general position.

As shown in Figure 22, the compound is a tetrahydroborate salt of the cation $[Li_2(H_2N\text{-}NHMe)_3]^{2+}$, which forms an infinite chain of Li atoms with each pair being bridged by two $H_2N\text{-}NHMe$ units. The BH_4 groups are placed above and below these chains (Figure 23). The Li–N bond lengths around the tetrahedrally coordinated Li1 atom are 2.082 (N3A) and 2.105(4) Å (N6A) and those at atom Li2 are 2.104(6) (N2B), 2.073(6) (N4B), 2.121(6) (N5B), and 2.057(6) Å (N1A). While most N–Li1–N angles are close to the tetrahedral angle [102.8(4)–109.7(1)], the angle N6A–Li1–N6 is exceptionally large [126.1(4)°]. The same holds true for the N–Li2–N angles. The N–N bond lengths fall in the range 1.437(4)–1.450(4) Å. As expected, the angles around the N atoms are close to 109.7°. The B–H bond lengths fall within the usual range.

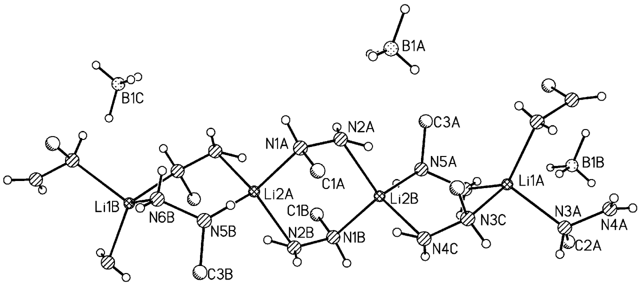

Figure 23. Structure of $[Li_2(H_2N\text{-}NHMe)_3](BH_4)_2$ (**14**). The BH_4 groups are arranged above and below the planes of the strands of six-coordinate Li ions with methylhydrazine molecules. Selected bond lengths [Å] and angles [°]: Li1A–N3A 2.082(5), Li1A–N6A 2.105(4), Li2A–N1A 2.057(6), Li2A–N4B 2.073(6), Li2A–N5B 2.121(6), Li2A–N2B 2.104(6), Li2B–N5A 2.121(6), Li2C–N4C 2.073(6), Li2A–N2B 2.104(6), N1A–N2A 1.437(4), N3A–N4A 1.449(4), N5B–N6B 1.450(4); N3A–Li1A–N3C 102.8(4), N3A–Li1A–N6A 109.7(1), N3C–Li1A–N6A 103.2(1), N6A–Li1A–N6C 126.1(4), N1B–Li2B–N2A 126.4(3), N4C–Li2B–N5A 104.1(2), N1B–Li2B–N2A 104.6(2), N1B–Li2B–N5A 108.6(3), N2A–Li2B–N5A 104.8(3).

In contrast, the adduct formed from $LiBH_4$ and $PhHN\text{-}NH_2$ has the composition $LiBH_4(H_2N\text{-}NHPh)_2$ (**15**). It crystallizes in the monoclinic system (space group *P*2$_1$/*m*) with *Z* = 4. There are two independent molecules in the unit cell. Figure 24 displays the atoms in the asymmetric unit. Both the Li atoms and the B atoms occupy special positions on the mirror plane. Each Li atom is six-coordinate to 2 N and 4 H atoms Adjacent Li atoms are bridged by a BH_4 group, which acts as a bis(bidentate) bridging unit. The Li–B distances are practically the same [Li1–B2B = 2.42(1), Li1–B1 = 2.45(1), Li2–B2 = 2.44(1), and Li2–B1C = 2.41(1) Å] and this is true also for the Li–N bonds. The N–N bond length is 1.417(5) Å (Figure 25).

As already indicated, the B–Li–B bond angles are 109.5°. While the N–Li–N bonds angles are, on average, 99.0°, the N–Li–B angles are more open at 115.4(3)° for N4A–Li1–B2B and 109.2° for N4–Li1–B2B and N4–Li1–B. The B2B–Li2B–B1A angle is 107.6(4)°.

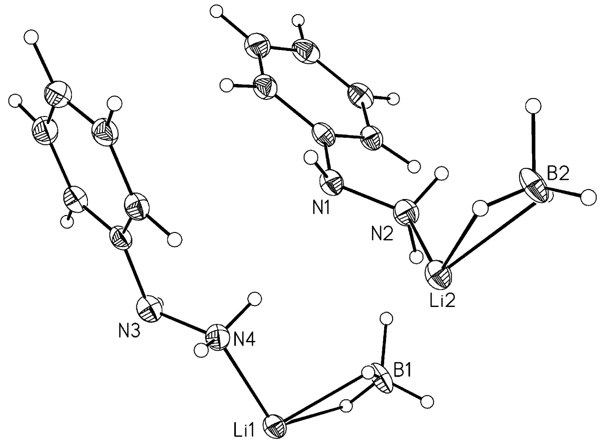

Figure 24. Atoms in the asymmetric unit of $LiBH_4(H_2N\text{-}NHPh)_2$ (**15**). Selected bond lengths [Å]: Li1–N4 2.064(7), Li2–N2 2.104(9), Li1–B1 2.45(1), Li2–B2 2.439(10), N1–N2 1.417(8), N3–N4 1.417(8), B1–H1A 1.16(4), B1–H1C 0.99(4), B1–H1D 0.94(4), B2–H2B 1.24(4), B2–H2A 1.08(4), B2–H2C 0.90(4).

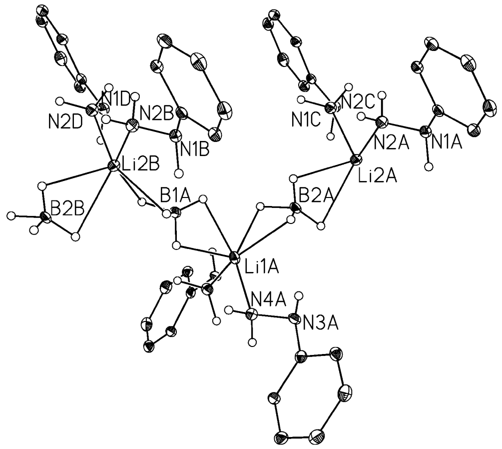

Figure 25. Part of the extended chain of $LiBH_4(H_2N\text{-}NHPh)_2$ (**15**). Selected bond lengths [Å] and angles [°]: Li1A–B2A 2.424(7), Li1A–N4A 2.064(7), B1A–Li2B 2.41(1), Li2A–B2A 2.44(1); N4–Li1A–N4A 99.4(4), N2–Li2–N2A 98.0(4), N4A–Li1A–B1A 109.2(3) B2A–Li1–B1A 107.6(4), B2A–Li1A–N4A 115.4(3).

Conclusions

The new structures of the coordination compounds of lithium, sodium, and potassium tetrahydroborates reported here, along with the already known structures, show the versatility of the BH_4 group as a ligand.

The B–H bond lengths change with the type of bonding situation and, in general, we observe short B–H bond lengths for terminal hydrogen atoms, longer ones for BH–M bridges, and even longer ones when the B(H) hydrogen atom is three- or even four-coordinate. However, the positions of the hydrogen atoms cannot be determined as precisely as those of the heavier atoms, therefore this trend is not always observed. Edelstein[15] has suggested to use the metal–boron distances as a criterion for the presence of a mono-, bi-, or tridentate BH_4 group because these distances can be determined more precisely. The longest M–B bond should be observed in compounds having only a single M–H–B bridging bond (corner-on bonding), and this distance should get shorter for bidentate $M(H)_2B$ bridges (edge-on bonding) and even shorter for tridentate-bonded BH_4 groups (face-on bonding). The data in Tables 1, 2, 3, and 4 show that this rule holds for mononuclear coordination compounds of the alkali metal tetrahydroborates. On the other hand, the differences in B–H bond lengths should become smaller as we move from the small Li cation to the larger Na cation and even larger K cation because polarization the BH_4 group by the metal cation will decrease as the radius of the metal increases.

Table 1. $LiBH_4$–ether adducts.

Compound	$CN_{(Li)}$	Li–B [Å]	B–H–Li type	B–H [Å]	B–H [Å]	Ref.
$[LiBH_4(OEt_2)]_n$	7	2.53 2.54	$3\mu_2^1$, $1\mu_4^3$	$B–H_1$ 1.12 $B–H_2$ 1.14	$B–H_3$ 1.01 $B–H_4$ 1.19	[5,6]
$LiBH_4$(thf)3	6	2.319	$3\mu_2^1$	$B–H_1$ 1.15[b] $B–H_2$ 1.15[b]		[15] [6]
$[LiBH_4(thf)]_n$	7	2.556 2.510 2.597 2.556	$3\mu_2^1$, $1\mu_4^3$	BH_A1.18 BH_B 1.12	BH_C 1.16 BH_D 1.05	[15]
$[LiBH_4(t\text{BuOMe})]_n$	7	2.560 2.505 2.529	μ_2^2, $2\mu_3^2$	$B–H_1$ 1.11 $B–H_2$ 1.12	$B–H_3$ 1.14 $B–H_4$ 1.11	[6]
$LiBH_4(DME)_2$	6	2.470	$2\mu_2^1$	$B–H_1$ 1.15	$B–H_2$ 1.17	[6]
$LiBH_4$(Triglyme)	6	2.486	$2\mu^2$	1.15	1.17	[6]
$[LiBH_4(Dioxolan)]_n$	6	2.446 2.431 2.426	$2\mu_2^2$	1.13 1.09	1.12 1.14	[6]
$[(OEt_2)_2LiBH_4]Ti_2(BH_4)_4$ $(PMe_2Ph)_4$	6	2.57 2.47	$2\mu_2^2$	1.16 (2x) 1.07(2x)	1.16 (2x) 1.07 (2x)	[16]
$LiBH_4$(15-crown-5)	8	2.608	$3\mu_2^1$	1.08, 1.09	1.15	[7]
$LiBH_4$(benzo–15-crown-5)	7	2.351	$2\mu_2^1$	1.07[b] 1.10	0.94, 1.06	[7]
$(LiBH_4)_2$(18-crown-6)	7	2.356 2.381	$1\mu_2^1$	1.07, 1.10	0.94, 1.04	[7]

However, Edelstein's rule is not predictive in polynuclear coordination compounds of the alkali metal tetrahydroborate, where the M–B distances are, in most cases, longer than in mononuclear species. The coordination number of the metal atom increases in these types of compounds, therefore the M–B distances increase irrespective of the type of M–H–B bonds present. Obviously, the effect of the increasing radius dominates.

From a structural point of view the polynuclear coordination compounds of the alkali metal tetrahydroborates are more interesting than the mononuclear species because of the different kinds of combinations of $M_n(H)_mB$ bonds. The

Table 2. $LiBH_4$–amine adducts.

Compound	CN($_{Li}$)	Li–B [Å]	Type	B–H	B–H	Ref.
$LiBH_4(py)_3$	5	2.401	$2\mu_2^1$	1.11, 1.10	1.09 t, 1.11 t	[9]
$LiBH_4(py\text{-}p\text{-}bzl)_3$	6	2.259	$3\mu_2^1$	1.08, 1.06	1.12, 1.24	[9]
		2.519				
$LiBH_4(py\text{-}4\text{-}Me)_3$	6	2.381	$3\mu_2^1$	1.12, 1.22	1.15, 1.08	this work
		2.319		1.14	1.07	
$[LiBH_4(py\text{-}2\text{-}Me)]_2$	6	2.517	$1\mu_3^2, 2\mu_2^1$	1.16, 1.12	1.18, 1.15	this work
		2.518				
$LiBH_4(py\text{-}2,4,6\text{-}Me_3)_2$	4	2.252	$2\mu_2^1$	1.17, 1.13		[9]
$LiBH_4(py\text{-}2\text{-}NH_2)(thf)_2$	5	2.419	$2\mu_2^1$	1.23, 1.24	1.14. 1.08	this work
		2.407		1.08, 1.13	0.95, 1.09	
$[LiBH_4(TMEDA)]_2$	6	2.467	μ_3^2, μ_2^2	1.19, 1.17	1.07, 1.06	[13]
		2.461				
$LiBH_4(PMDTA)$	5	2.286	$2\mu_2^1$	1.07, 1.07	1.31, 1.30	[9]
		2.346		1.22, 1.21	0.95, 0.94	
$[LiBH_4(MeNCH_2)_3]_2$	6	2.395	$1\mu_3^2, 2\mu_2^1$	1.14 br. s	1.13 t	[9]
				1.15 br. t	1.15 br. s	
$LiBH_4(H_2NPh)_3$	6	2.260	$3\mu_2^1$	0.86, 1.10	0.89, 0.94	[9]
		2.363				
$[(LiBH_4)_3(H_2N\mathit{t}Bu)_4]_n$	5	2.476	$2\mu_3^2, 2\mu_2^1$	1.14, 1.14	1.14, 1.14	this work
	5	2.609		1.18, 1.15	1.16, 1.18	
	6	2.500	$2\mu_2^1$	1.00, 1.06	1.13, 1.14	
		2.404	$2\mu_2^1$			
		2.382	$\mu_2^{1'}$			
$LiBH_4(H_2NCH_2CH_2)NH$	6	2.336	$3\mu_2^1$	1.17, 1.11	1.03, 1.15	[16]
$[LiBH_4(HNC_4H_8)]_n$	7	2.561	μ_4^3, μ_2^3	1.08–1.15	1.05–1.14	[16]
		2.530				
		2.527				
		2.569				
$[LiBH_4(HNbzl_2)_2]_2$	6	2.516	μ_2^2, μ_3^2	1.09, 1.17	1.13, 1.14	[16]
		2.467				
$[LiBH_4(HN\mathit{i}Pr_2)]_n$	5	2.358	μ_3^2	1.06, 1.08	1.04, 1.17	[16]
		2.359	$2\mu_2^1$			
$[LiBH_4(HN\mathit{i}Bu_2)]_n$	7	2.542	$3\mu_3^2$	1.10, 1.12	1.06, 1.12	this work
		2.543	$1\mu_2^1$	0.98, 1.14	1.09, 1.09	
$[LiBH_4(\mathit{i}PrNCH_2)_3]_2$	7	2.422	$\mu_3^2, 2\mu_2^1$	1.14, 1.12		[8]
		2.525		1.14		
$[(LiBH_4)_4\ \{(MeNCH_2)_3\}_2]$	Li_1:6	2.428	B1: $2\mu_2^2$	1.14	1.19	[8]
	Li_2:6	2.381	B2: $2\mu_2^2$	1.11	1.12	
	Li_3:7	2.302	B3: 4 μ_2^1	1.14	1.05	
	Li_4:6	2.369	B4: $2\mu_2^2$	1.10	1.13	
$[LiBH_4(bzlNCH_2)_3]$	6	2.355	$1\mu_3^2, \mu_2^1$	1.16, 1.15	1.18, 1.22	[8]
$Li_2(BH_4)_2$						
	6	2.381		1.12, 2.14	0.94, 1.00	
	6		μ_2^1	1.11, 1.14	1.16	
$[LiBH_4(H_2NNHPh)_2]_n$	6	2.41	μ_3^2, μ_2^2	1.16, 0.99	1.24, 1.08	this work
		2.42		0.94, 1.16	0.90, 1.24	
		2.43				
		2.41				
$LiBH_4(N\text{-}2,4\text{-}Me_2pz)_3CH$	6	2.223	$3\mu^1$	1.29	0.79	[17]
				0.79	0.79	
$[LiBH_4\{(N\text{-}2,4\text{-}Me_2pz)$ $_2CH_2\}_2]$	6	2.259	$3\mu_2^1$	1.08	1.20	[18]
			$\mu_2^{1'}$	1.06	1.13	
$[LiBH_4(4,7\text{-}Me_2dipy)]_2$	6	2.479	$1\mu_3^2, 2\mu_2^2$	1.03	1.02	[18]
		2.407		1.02	1.02	
		2.417				
		2.498				

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Table 3. $NaBH_4$ adducts.

Compound	CN($_{Na}$)	Na–B [Å]	Type	B–H [Å]	B–H [Å]	Ref.
$[NaBH_4]_2$(triglyme)	8	2.807	$1\,\mu_4{}^3$			this work
		2.830				
		2.869	$\mu_2{}^3$			
		2.880				
		2.860				
		2.905				
$NaBH_4$(15-crown-5)$(py)_{0.5}$	7	2.659	$2\,\mu_2{}^1$	1.04, 1.16	1.12, 1.18	this work
$NaBH_4$(15-crown-5)	7	2.608	$3\,\mu_2{}^1$	1.15, 1.09	1.04, 1.08[a]	[16]
$NaBH_{4r}(morpholine)_2$	6	3.388	$2\,\mu_2{}^1$			this work
	7	3.392				
	7	2.652	$3\,\mu_2{}^1$			
	7	2.642	$3\,\mu_2{}^1$			
		2.637				
		2.908	$2\,\mu_2{}^1$			
		2.907	$2\,\mu_2{}^1$			
$[NaBH_4(py)_3]_2$	9	2.865	$1\,\mu_3{}^2$	1.05	1.06	this work
		3.047	$2\,\mu_2{}^2$	1.09	1.13	
$[NaBH_4(bzlNH_2)]_2$	5	2.865				this work
		3.047				
$[NaBH_4(HCpz_3)THF]_2$	6	2.985	$2\,\mu_2{}^{1,1}$	1.12, 1.03	1.16	[17]
		2.864	$2\,\mu_2{}^{2,2}$		1.12	
$[NaBH_4(PMDTA)]_2$		2.867	$\mu_3{}^2$, $\mu_2{}^2$	1.10, 113	0.97, 0.08	this work
$[NaBH_4(MeNC_3H_6)_3]_4$	9	3.114	$\mu_4{}^3$, $\mu_2{}^3$	1.14, 1.26		[9]

Table 4. KBH_4 solvates.

Compound	CN($_K$)	K–B [Å]	Type	B–H	B–H	Ref.
KBH_4(18-crown-6)	9	2.964	$3\,\mu_2{}^1$	0.98, 1.08	1.02, 1.11	[16]
KBH_4(18-crown-6)	9	2.947	$3\,\mu_2{}^1$	1.12, 1.15	1.12, 1.03	this work
KBH_4(benzo-18-crown-6)	9	2.993, 2.756	$3\,\mu_2{}^1$	1.15, 1.15	1.15, 1.15	[2]

most striking example is provided by $NaBH_4(morpholine)_2$, with its combination of $\mu_2{}^1$, $2\,\mu_2{}^2$, and $3\,\mu_2{}^1$ bridges. This example shows that coordination compounds of $NaBH_4$ and KBH_4 are candidates for structures with new combinations of coordinated BH_4 groups.

Experimental Section

All manipulations were performed under an atmosphere of either argon or nitrogen using Schlenk techniques. Solvents were dried by standard procedures. The amines used were commercial products and the alkali metal tetrahydroborates were received from Chemetal. NMR: Jeol 400, external reference $BF_3{\cdot}OEt_2$ or ext. aqueous 1 M LiCl. X-ray diffraction: Siemens P4 four circle diffractometer equipped with an area detector and a LT device, Mo-K_α radiation, graphite monochromator. The thermal ellipsoids shown in the figures are depicted at a 25% probability level.

$LiBH_4$(thf) (1): A 1 M solution of $LiBH_4$ in THF (50 mL) was reduced in vacuo to about 4 mL, then 10 mL of *n*-hexane was added and the solution heated to 50 °C at 10 Torr to remove more THF. Methylcyclohexane (10 mL) was then added to the resulting viscous liquid and the turbid solution stored at –10 °C. The colorless hygroscopic crystals that formed within a few days were isolated by filtration at 0 °C. Yield: 2.6 g (52%). Elemental analysis gave erratic results due to loss of coordinated THF. The crystal structure determination (selecting the crystal at –20 °C) showed that the compound had the composition $LiBH_4$(thf).

$NaBH_4(C_8H_{18}O_4)$ (2): $NaBH_4$ (1.20 g, 31.7 mmol) was added to triglyme (25 mL). After stirring for 1 h the turbid solution was filtered and the filtrate was reduced to half of its volume at 50 °C/0.1 Torr. Methylcyclohexane (5 mL) was then added to the remaining solution, which was stored at –5 °C. Crystals separated within a few days. Yield: 4.5 g (65.7%). The crystals are hygroscopic. ^{11}B NMR (triglyme): δ = –41 ppm (quint, $^1J_{^{11}B,^1H}$ = 81 Hz). $C_8H_{22}BNaO_4$ (216.06): calcd. C 44.47, H 10.26; found C 43.98, H 10.06.

$NaBH_4$(15-crown-5)$(NC_5H_5)_{0.5}$ (3): $NaBH_4$ (80.6 mg, 2.13 mmol) was suspended in 15-crown-5 (500 mg, 2.27 mmol) and then pyridine (8 mL) was added to give a clear solution, which was then treated with methylcyclohexane (2 mL). A colorless precipitate formed within a few hours. After filtration the filtrate was stored at 8 °C. Crystals separated within two weeks. Yield: 393 mg (31%), m.p. 109–112 °C. ^1H NMR (C_6D_6): δ = 0.8 ppm (q, $^1J_{^{11}B,^1H}$ = 81 Hz; sept. $^1J_{^{10}B,^1H}$ = 27 Hz). ^{11}B NMR: δ = –41.1 ppm (quint, $J_{^{11}B,^1H}$ = 81 Hz). $C_{25}H_{53}B_2NNa_2O_{10}$ (595.38): calcd. C 50.44, H 8.97, N 2.35; found C 49.35, H 9.00, N 1.89.

$[Na(18\text{-crown-}6)(NC_5H_5)_2]BH_4$ (4): $NaBH_4$ (36 mg, 0.96 mmol) was mixed with 18-crown-6 (267 mg, 1.09 mmol) and this mixture dissolved in pyridine (5 mL). The colorless precipitate that formed upon addition of methylcyclohexane (4 mL) was isolated by filtration. Storing the filtrate at 4 °C yielded colorless needles within a few days. Yield: 150 mg (34%), m.p. 92–94 °C. ^{11}B NMR (pyridine): δ = –40.7 ppm (quint, $^1J_{^{11}B,^1H}$ = 81 Hz). IR (Nujol, BH region): $\tilde{\nu}$ = 2283 (m), 2210 (st), 2146 (m) cm^{-1}. $C_{22}H_{38}BN_2NaO_6$

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(460.27): calcd. 57.40, H 8.32, N 6.09; found C 56.43, H 8.29, N 6.20.

KBH_4(18-crown-6) (5): KBH_4 (34 mg, 0.64 mmol) and toluene (15 mL) were added to a stirred solution of 18-crown-6 (170 mg, 0.69 mmol) in pyridine (10 mL). The solution was stored at 8 °C and colorless needles separated within a few days. Yield: 46.9 mg (23%), m.p. 220 °C. ^{11}B NMR (C_6D_6): δ = –39.2 ppm (quint, $^1J_{^{11}B,^1H}$ = 81 Hz). IR (Nujol, BH region): $\tilde{\nu}$ = 2299 (st), 2242 (sh), 2218 (st), 3275 (st, 2140 sh) cm^{-1}. $C_{12}H_{28}BKO_6$ (318. 6): calcd. C 45.29, H 8.87; found C 45.26, H 9.03.

$K(H_2BC_5H_{10})$(18-crown-6) (6): Potassium dihydroborinate·3thf[14] (0.4 g, 1 mmol) was dissolved in thf (50 mL) and addition of 18-crown-6 (0.5 g, 2 mmol) to this solution gave a colorless precipitate. After filtration the filtrate was kept at 8 °C. The compound separated within a few days as colorless prisms. The yield was not determined. M.p. 167–170 °C (dec.). ^{11}B NMR (thf): δ = –19.9 ppm (t, $^1J_{^{11}B,^1H}$ = 74 Hz). IR (Nujol): $\tilde{\nu}$ = 2182 (m), 2143 (st), 2109 (st), 2064 (w), 2047 (st), 1474 (s st), 1459 (st), 1437 (st), 1352 (st), 1285 (sh), 1252 (st), 1213 (m), 1138 (sh), 1104 (st), 963 (st), 838 (st) cm^{-1}. $C_{17}H_{36}BKO_6$ (386.22): calcd. C 52.85, H 9.39; found C 52.65, H 10.25.

$LiBH_4(NC_5H_4\text{-}4\text{-}Me)_3$ (7): $LiBH_4$ (257 mg, 11.8 mmol) was suspended in 4-picoline (30 mL), and subsequent addition of methylcyclohexane (10 mL) gave a turbid solution. The solid was removed by filtration and the filtrate stored at –20 °C. Colorless prismatic crystals separated within a few days. Yield: 2.38 g (67%), m.p. 40 °C (dec.). ^{11}B NMR (4-picoline): δ = –39.2 ppm ($^1J_{^{11}B,^1H}$ = 82 Hz). ^{7}Li NMR (4-picoline): δ = 2.4 ppm. IR (Nujol, BH region): $\tilde{\nu}$ = 2321 (sh), 2251 (st), 2181 (sh) cm^{-1}. $C_{18}H_{25}BLiN_3$ (304.13): calcd. C 71.08, H 8.28, N 14.79; found C 71.11, H 8.46, N 13.78.

$[LiBH_4(NC_5H_4\text{-}2\text{-}Me)_2]_2$ (8): $LiBH_4$ (223 mg, 10.2 mmol) was added to 2-methylpyridine (25 mL) while stirring and then methylcyclohexane (10 mL) was also added. After 2 h the mixture was filtered and the filtrate was kept at 8 °C. Colorless prismatic crystals separated within one day. Yield: 894 mg (42%); m.p. 34 °C (dec.). ^{11}B NMR (2-picoline): δ = –39.0 ppm ($^1J_{^{11}B,^1H}$ = 80 Hz). ^{7}Li NMR: δ = 2.1 (s), 2.4 ppm (s; 1:1). Selected IR data (Nujol, BH region): $\tilde{\nu}$ = 2383 (m), 2327 (st), 2284 (sh), 2186 (st) cm^{-1}. $C_{12}H_{18}BLiN_2$ (210.21): calcd. C 68.56, H 8.63, N 14.26; found C 67.45, H 8.81, N 12.93.

$LiBH_4(py\text{-}2\text{-}NH_2)(thf)_2$ (9): A solution of $LiBH_4$ (107 mg, 5.03 mmol) in THF (20 mL) was added to a solution of 2-aminopyridine (465 mg, 4.80 mmol) in THF (30 mL). After 30 min the turbid mixture was filtered and the volume of the filtrate reduced in vacuo to about 20 mL. Colorless prisms separated from this solution within one hour. Yield: 900 mg (70%), m.p. 48–50 °C. ^{11}B NMR ($CDCl_3$): δ = –42.0 ppm (sh). ^{7}Li NMR: δ = 0.50 ppm. ^{1}H NMR: δ = 8.07 (d), 6.59 (dd), 7.51 (t), 3.75 (thf), 1.75 (thf), –0.3 ppm (q, BH_4). ^{13}C NMR: δ = 155.4, 140.0, 113.0, 112.2, 67.5, 25.4 ppm. IR (KBr BH region): $\tilde{\nu}$ = 1641.9 sh, 1602.2 (st), 2303 cm^{-1} (br); (NH region): $\tilde{\nu}$ = 3467 (st), 3361 cm^{-1} (st). $C_{13}H_{26}BLiN_2O_2$ (260.11): calcd. C 60.06, H 10.08, N 10.78; found C 59.50, H 9.56, N 10.65.

$NaBH_4(py)_3$ (10): $NaBH_4$ (234 mg, 6.43 mmol) was partially dissolved in a mixture of pyridine (10 mL) and toluene (10 mL). After stirring for several hours the suspension was filtered and the filtrate stored at –35 °C. The needles that had formed after several days were isolated by filtration. The compound melts at about –10 °C with decomposition (formation of a liquid and solid phase). ^{11}B NMR (pyridine): δ = –40.4 ppm (quint. $^1J_{^{11}B,^1H}$ = 81 Hz). $C_{15}H_{19}BN_3Na$ (275.16): calcd. C 65.48, H 6.96, N 15.27; found C 65.24, H 7.03, N 15.48.

$LiBH_4(HN\mathit{i}Pr_2)$ (11): Diisopropylamine (5.3 mL, 45 mmol) was added to a stirred solution of $LiBH_4$ in THF (0.98 g, 45 mmol, 15 mL). The suspension that had formed after 1 h was kept for 15 min at 45 °C and then the insoluble material was removed by filtration. methylcyclohexane (2 mL) was added to the filtrate and the solution stored at –5 °C. Colorless crystals separated within 2 days. The crystals melted at 0 °C. Yield: 4.04 g (73%). No satisfactory elemental analysis was obtained due to deterioration of the liquid at room temperature. ^{11}B NMR (C_6D_6): δ = –39.8 ppm. ^{7}Li NMR: δ = –0.5 ppm. IR (Nujol, BH region): $\tilde{\nu}$ = 2304 (st), 2280 cm^{-1} (st).

$LiBH_4(HN\mathit{i}Bu_2)$ (12): Diisobutylamine (5 mL) was added to a solution of $LiBH_4$ (350 mg, 16.1 mmol) in THF (15 mL) and the mixture was kept for 10 min at 40 °C. After filtration hexane (2 mL) was added and the solution stored at 5 °C. Needles formed within one day. Yield: 180 mg (40%), m.p. 80–83 °C. ^{11}B NMR (thf): δ = –41.2 ppm (quint, $^1J_{^{11}B,^1H}$ = 83 Hz). ^{7}Li NMR: δ = –0.31 ppm. $C_8H_{23}BLiN$ (152.01): calcd. C 63.62, H 15.35, N 9.27; found C 62.34, H 15.25, N 8.49.

$NaBH_4[HN(CH_2CH_2)_2O]_2$ (13): Methylcyclohexane (4 mL) was added to a saturated solution of $NaBH_4$ in morpholine (20 mL). Large colorless needles crystallized within a few hours. M.p. 31 °C (dec.). The crystals deteriorated at room temperature, therefore erratic data were obtained in elemental analysis. However, when the crystals were manipulated below –20 °C they could be easily handled. The X-ray structure determination proved the composition of the crystals. ^{11}B NMR (morpholine): δ = –41.8 ppm (quin. $^1J_{^{11}B,^1H}$ = 81 Hz). IR (Nujol, BH region): $\tilde{\nu}$ = 2409 (m), 2314 (st), 2251 (st), 2185 (sh), 2182 cm^{-1} (m).

$(LiBH_4)_2(H_2N\text{-}NHMe)_3$ (14): Methylhydrazine (1.3 mL, 26.8 mmol) was added to a solution of $LiBH_4$ (536 mg, 25.2 mmol) in THF (15 mL). After a few minutes a white solid formed. The suspension was then kept for 5 min at 50 °C and the resulting clear solution was stored at 5 °C. Colorless prismatic crystals formed within one day. Yield: 100 mg (68%), m.p. 54–56 °C. ^{11}B NMR (THF): δ = –41.7 ppm (quint, $^1J_{^{11}B,^1H}$ = 81 Hz). ^{7}Li NMR: δ = 2.75 ppm. $C_3H_{24}B_2Li_2N_6$ (175.75): calcd. C 20.27, H 13.46, N 46.23; found C 21.09, H 13.63, N 45.85

$LiBH_4(H_2N\text{-}NHPh)_2$ (15): Phenylhydrazine (5.25 g, 4.8 mL, 39.8 mmol)) was added dropwise, with stirring, to a solution of $LiBH_4$ (0.866 g, 39.8 mmol) in THF (20 mL). Crystals separated from the solution within two days at 5 °C. Yield: 2.3 g (48%); m.p. 138–140 °C. ^{11}B NMR (C_6D_6): δ = –43.0 ppm (quint, $^1J_{^{11}B,^1H}$ = 82 Hz). ^{7}Li NMR: δ = 1.7 ppm. IR (Nujol, BH region): $\tilde{\nu}$ = 2495 (w), 2417 (w), 2377 (m), 2335 (st), 2288 (st), 2248 (st), 2223 cm^{-1} (m). $C_{12}H_{20}BLiN_4$ (238.82): calcd. C 60.35, H 8.44, N 23.46; found C 59.65, H 8.29, N 22.93.

Structure Determinations: As a precaution, the selection of suitable single crystals was performed under nitrogen gas cooled to –25 °C. The crystals were placed in pre-cooled perfluoro ether oil and the selected crystal was then mounted on the top of a glass fiber. The goniometer head was flushed with nitrogen gas cooled to –80 °C. After alignment, data were collected on five sets of 15 frames each by changing ω in 0.5° steps. Cell dimensions were calculated from the reflections of these frames. Data collection was performed in the hemisphere mode. All reflections of 1200 frames were used for the structure solutions. Data reduction was performed with the program SMART, and structure solution and refinement with the programs implemented in SHELX-93 or SHELXTL. The positions of the boron- and nitrogen-bonded H atoms were refined freely, while those bonded to the C atoms were placed in calculated positions and treated as riding on the C atoms. The Flack parameters

Table 5. Crystallographic and structure solution and refinement data for compounds **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_4H_{12}BLiO$	$C_8H_{26}B_2Na_2O_4$	$C_{25}H_{53}BNNa_2O_{10}$	$C_{22}H_{34}BN_2NaO_6$	$C_{12}H_{28}BKO_6$
Formula weight	93.89	253.89	595.28	460.27	318.25
Crystal size [mm]	0.36 × 0.40 × 0.45	0.25 × 0.33 × 0.4	0.22 × 0.27 × 0.34	0.05 × 0.40 × 0.60	0.10 × 0.10 × 0.50
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a [Å]	4.5354(9)	12.216(2)	7.74(1)	8.803(1)	8.2230(1)
b [Å]	11.040(2)	9.6207(19)	14.43(2)	14.020(2)	12.034(2)
c [Å]	13.342(3)	15.982(3)	15.27(2)	10.676(2)	17.985(3)
α [°]	90	90	90	90	90
β [°]	99.40(3)	112.11(3)	100.31(3)	97.991(2)	90
γ [°]	90	90	90	90	90
V [Å^3]	659.1(2)	1740.3(6)	1678(4)	1304.8(3)	1779.7(4)
Z	4	4	2	2	4
ρ(calcd.) [Mg m^{-3}]	0.946	0.969	1.178	1.161	1.188
μ [mm^{-1}]	0.058	0.111	0.108	0.097	0.316
F(000)	208	552	644	488	688
Index range	$-3 \le h \le 3$	$-9 \le h \le 16$	$-10 \le h \le 6$	$-10 \le h \le 10$	$-10 \le h \le 10$
	$-13 \le k \le 13$	$-10 \le k \le 12$	$-17 \le k \le 17$	$-18 \le k \le 8$	$-14 \le k \le 15$
	$-16 \le l \le 16$	$-20 \le l \le 16$	$-19 \le l \le 18$	$-12 \le l \le 12$	$-23 \le l \le 23$
2θ [°]	54.74	57.50	56.22	56.06	57.38
Temperature [K]	213	193	193	183(2)	183.(2)
Reflections collected	3604	3667	8499	6598	10356
Reflections unique	1017	2047	2821	1941	3768
Reflections observed (4σ)	602	1721	1898	1500	1967
R(int.)	0.0535	0.0680	0.0235	0.0197	0.1344
Number of variables	80	117	213	148	198
Weighting scheme x/y[a]	0.1376/0.0552	0.0733/0.7968	0.0516/0.0	0.0911/0.1151	0.0955/0.1754
GOOF	1.116	1.048	0.953	1.080	1.009
Final R (4σ)	0.0663	0.0454	0.0341	0.0465	0.0853
Final wR_2	0.2069	0.1186	0.0797	0.1320	0–1472
Largest resid. peak [e Å^3]	0.211	0.389	0.141	0.358	0.367

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

Table 6. Crystallographic and structure solution and refinement data for compounds **6**–**10**.

	6	**7**	**8**	**9**	**10**
Empirical formula	$C_{34}H_{72}B_2K_2O_{12}$	$C_{36}H_{50}B_2Li_2N_6$	$C_{12}H_{18}BLiN_2$	$C_4H_{12}BLiO$	$C_{15}H_{19}BN_3Na$
Formula weight	772.74	602.32	208.03	93.89	275.13
Crystal size [mm]	0.20 × 0.20 × 0.60	0.2 × 0.2 × 0.4	0.20 × 0.30 × 0.30	0.36 × 0.40 × 0.45	0.40 × 0.40 × 0.50
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$Pbca$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a [Å]	8.5768(7)	15.2419(9)	8.997(2)	4.5354(9)	9.6253(7)
b [Å]	14.058(1)	19.968(18)	13.497(3)	11.040(2)	9.7190(7)
c [Å]	18.028(2)	25.698(2)	11.283(3)	13.342(3)	17.511(1)
α [°]	94.086(2)	90	90	90	90
β [°]	90.323(1)	90	102.015(5)	99.40(3)	90
γ [°]	93.811(1)	90	90	90	90
V [Å^3]	2162.4(3)	7821.0(9)	1340.2(6)	659.1(2)	1638.1(2)
Z	2	8	4	4	4
ρ(calcd.) [Mg m^{-3}]	1.187	1.023	1.031	0.946	1.116
μ [mm^{-1}]	0.272	0.059	0.059	0.058	0.089
F(000)	840	2592	448	208	584
Index range	$-10 \le h \le 10$	$-11 \le h \le 19$	$-9 \le h \le 9$	$-3 \le h \le 3$	$-12 \le h \le 12$
	$-14 \le k \le 17$	$-24 \le k \le 24$	$-14 \le k \le 14$	$-13 \le k \le 13$	$-12 \le k \le 12$
	$-23 \le l \le 23$	$-32 \le l \le 31$	$-11 \le l \le 11$	$-16 \le l \le 16$	$-19 \le l \le 23$
2θ [°]	58.26	52.74	46.46	54.74	57.86
Temperature [K]	193(2)	193(2)	188(2)	213	183(2)
Reflections collected	12523	41823	5742	3604	9477
Reflections unique	6559	7104	1722	1017	3400
Reflections observed (4σ)	4941	3996	1443	602	2803
R(int.)	0.0293	0.0608	0.0382	0.0535	0.0747
Number of variables	483	454	152	80	197
Weighting scheme x/y[a]	0.0578/0.3036	0.0722/1.9354	0.1062/0.3605	0.1376/0.0552	0.071/0.1226
GOOF	1.012	1.047	1.034	1.116	1.063
Final R (4σ)	0.0406	0.0564	0.0593	0.0663	0.0536
Final wR_2	0.1003	0.1355	0.1567	0.2069	0.1228
Larg. res. peak [e Å^3]	0.217	0.191	0.228	0.211	0.182

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

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Table 7. Crystallographic and structure solution and refinement data for compounds **11**–**15**.

	11	**12**	**13**[12]	**14**	**L15**
Empirical formula	$C_6H_{19}NBLi$	$C_8H_{23}BLiN$	$C_8H_{22}N_2NaO_2$	$C_3H_{24}B_{1.50}Li_{1.50}N_6$	$C_{12}H_{20}BLiN_4$
Formula weight	122.97	151.02	212.08	170.91	238.07
Crystal size [mm]	0.4 × 0.45 × 0.56	0.3 × 0.36 × 0.65	0.3 × 0.2 × 0.1	0.18 × 0.22 × 0.25	0.31 × 0.55 × 0.46
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_1$	$C2/c$	$P2_1/m$
a [Å]	7.7837(8)	22.189(7)	11.5302(5)	9.863(2)	5.569(2)
b [Å]	6.8563(8)	15.603(5)	14.3647(5)	13.634(3)	30.89(1)
c [Å]	18.707(2)	6.611(2)	14.6638(6)	17.906(4)	7.874(3)
α [°]	90	90	90	90	90
β [°]	101.895(2)	90.50(6)	90.05(2)	99.49(3)	90
γ [°]	90	90	90	90	90
V [Å^3]	976.9(2)	22889(1)	2428.73	2375.0(8)	1354.6(8)
Z	4	8	8	8	4
ρ(calcd.) [Mg m^{-3}]	0.836	0.877	1.160	0.956	1.167
μ [mm^{-1}]	0.045	0.047	0.110	0.061	0.070
F(000)	280	688	928	768	512
Index range	$-7 \le h \le 7$	$-28 \le h \le 28$	$-14 \le h \le 14$	$-11 \le h \le 11$	$-7 \le h \le 6$
	$-8 \le k \le 8$	$-19 \le k \le 19$	$-14 \le k \le 18$	$-16 \le k \le 15$	$-30 \le k \le 29$
	$-24 \le l \le 24$	$-5 \le l \le 5$	$-19 \le l \le 19$	$-13 \le l \le 21$	$-10 \le l \le 10$
2θ [°]	55.26	55.56	58.08	50.10	55.24
Temperature [K]	203	203	183	193	193
Reflections collected	5237	12585	13980	9205	7334
Reflections unique	1668	3487	8953	2084	2450
Reflections observed (4σ)	1126	1239	7408	1502	1667
R(int.)	0.2035	0.1969	0.0231	0.0573	0.1196
Number of variables	158	229	578	142	254
Weighting scheme x/y[a]	0.0833/0.000	0.1196/0.0	0.0376/0.5807	0.1562/5.607	0.0214/1.7342
GOOF	1.050	0.873	1.074	1.048	1.221
Final R (4σ)	0.0579	0.0769	0.0437	0.0869	0.0849
Final wR_2	0.1750	0.1849	0.0930	0.2508	0.1906
Larg. res. peak [e Å^3]	0.168	0.176	0.192	0.613	0.263

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

(0 ± 0.3) supported the calculations for the noncentrosymmetric space groups. CH hydrogen atoms are not shown in all figures. Tables 5, 6, and 7 displays relevant results for crystallographic data and data related to structure solution.

CCDC-653996 (compound **1**), -653997 (compound **2**), -653998 (compound **3**), -653999 (compound **4**), -654000 (compound **5**), -654001 (compound **6**), -654002 (compound **7**), -654003 (compound **8**), -654004 (compound **9**), -654005 (compound **10**), -654006 (compound **11**), -654007 (compound **12**), -654008 (compound **13**), -654009 (compound **14**), and -654010 (compound **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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